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Charging poly(methyl methacrylate) latexes in nonpolar solvents: Effect of particle concentration

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Abstract

The electrophoresis of dispersions of poly(12-hydroxystearic acid)-stabilized poly(methyl

methacrylate) latexes in dodecane charged by Aerosol OT surfactant, a well-established model system of charged colloids in nonpolar solvents, has been studied as a function of particle volume fraction at constant surfactant concentration, a variable that has heretofore not been explored. The electrophoretic mobility (μ) of the PMMA latexes is found to decrease as the particle concentration increases. As the particles are charged by an external charging agent at finite concentration, the origin of this is unclear; it could be due either due to the reservoir of available surfactant being exhausted at high particle concentrations or the double layers of the charged particles overlapping at high particle number concentrations. Contrast-variation small-angle neutron scattering measurements of PMMA latexes and deuterated AOT-d_{34} surfactant in latex core contrast-matched solvent were used to study the former, and electrokinetic modeling were used to study the latter. As the same amount of AOT-d_{34} is found to be incorporated with the latexes at all volume fractions, the overlap of double layers is determined to be explanation for the decrease in mobility. These measurements show that, for small latexes, double layers overlap at all accessible particle volume fractions and that it is necessary to account for this to accurately determine the electrokinetic ζ potential.

Introduction

Producing charged particles in nonpolar, hydrocarbon solvents is well-known to be a challenging problem; however, when successfully produced, charged species have a wide range of uses in many industries.[1–4] It is difficult to stabilize charged species in nonpolar solvents, such as dodecane, due to the low relative permittivity, or dielectric constant, of the fluid ($\epsilon_r = 2.0120$) compared to that of a polar solvent such as water ($\epsilon_r = 80.100$). (Both ϵ_r values are at 20°C.[5]) This can be well understood by considering the Bjerrum length (λ_B) of the medium (Equation 1), the separation between two point charges where the Coulombic interaction is equal to the thermal energy (k_BT), which depends on the elementary charge

(e), the vacuum permittivity (ϵ_0), ϵ_r, and k_BT.

$$\lambda_B = \frac{e^2}{4\pi\epsilon_0\epsilon_r k_B T} \tag{1}$$

In water, λ_B is $\sim$ 1 nm, which is why ions can be easily stabilized in the solvent. In hydrocarbon solvents, λ_B is $\sim$ 30 nm, which means that dissociation fractions are low for moderately sized ions[6–11] or that very large diffuse ions must be used to attain high dissociation fractions.[12]

Poly(methyl methacrylate) (PMMA) latexes with poly(12-hydroxystearic acid) (PHSA) graft copolymer stabilizer layers, developed in collaboration between the University of Bristol and ICI in the 1980s,[13] have long been established as a model system for studying interactions in nonpolar solvents. Since it was reported in 2005 that these latexes could be charged by sodium dioctylsulfosuccinate (Aerosol OT or AOT) surfactant,[14] these particles have been increasingly used as a model for studying the nature of charged colloids in nonpolar solvents.[8,10,11,15–25] From all the studies in the literature on these particles, the impact of systematically varying many of parameters of the system (such as particle size, surfactant concentration, surfactant polarity, and surfactant counterion) and the impact on the charge of the particle has been studied.[26] However, one of the variables that can impact the electrophoresis of charged particles has surprisingly not been reported for PMMA latexes charged by AOT: the particle volume fraction. This variable has been studied for other methods of charging PHSA-stabilized PMMA, by either the incorporation of a polymerizable ionic monomer[27] or by dispersing the particles in an autoionizable solvent.[28] The effect of varying volume fraction has been studied for AOT charging of other types of polymer particles,[29,30] although only simple analysis of the electrophoresis data was performed. For AOT-charged PMMA latexes, the situation is complex as the ratio of the particle volume fraction to the surfactant volume fraction will increase as the dispersions are concentrated, at a fixed surfactant concentration. Therefore, it is possible that the reservoir of surfactant

could be depleted. However, it is also known from the literature that the electrophoretic mobility will decrease in concentrated dispersions, even at constant ζ potential, due to the overlapping of the electrical double layers.[31–35] Despite these possible impacts of increasing the volume fraction, changing this variable is an important one to study. For these charged colloids to be employed in an industrial setting, they will need to be used efficiently by loading the greatest concentration in dispersion as is possible.

In this paper, the functional and structural properties of dispersions of PHSA-stabilized PMMA latexes charged by AOT in dodecane have been studied as a function of particle volume fraction (ϕ). The charge of the particles was measured using electrophoretic light scattering, specifically phase-analysis light scattering (PALS). The interaction between particles and the distribution of AOT were studied using small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS). Together these measurements reveal the impact that concentrating these dispersions has on the charge of the particles. The focus is primarily on very small latexes, which are required for the SAXS and SANS experiments; these particles also tend to have a lower ζ potential, which has been observed in the literature,[26] although not fully understood. By considering how the electrophoretic and structural properties vary as a function of particle concentration, it has been possible to determine the origin of any differences. This will impact both fundamental studies of these particles as model charged colloids and industrial applications of them as concentrated dispersions.

Experimental section

Materials

Aerosol OT surfactant

Commercial sodium dioctylsulfosuccinate (Aerosol OT or AOT) was obtained from Aldrich (98%) and was purified using dry diethyl ether before use. The synthesis and analysis of

deuterium labeled AOT-d_{34} has previously been reported.[23]

PMMA latexes

GS1 and SF1 latexes were prepared by a classic dispersion polymerization process using the method described by Antl *et al.*[13] The synthetic procedure is provided elsewhere.[36] MC1 latexes were a gift from Merck Chemicals Ltd. The Z-average solvodynamic diameters (d_Z) and polydispersity indexes (PdIs) of the latexes were measured using a Malvern ZetaSizer Nano S90: GS1 ($d_Z = 76.1 \pm 0.5$ nm, PdI= 0.11), MC1 ($d_Z = 412 \pm 5$ nm, PdI= 0.07), and SF1 ($d_Z = 666 \pm 24$ nm, PdI= 0.13).

Volume fractions were determined by drying suspensions to determine the mass of dry particles in suspension. The mass densities (ρ_m) of dodecane ($\rho_m = 0.75$ g cm^{-3})[37] and the PMMA latexes were used to convert the masses to densities to work out the volume fraction; this is the approach used by Pusey and van Meegan in their early papers on the phase behavior of PMMA latexes.[38,39] The mass density of the latexes is a function of their size, as the PHSA stabilizer makes up a different fraction of the total volume. The core density of the latex is effectively independent of the particle size, although less than the density of PMMA homopolymer,[36] and the density of the PHSA stabilizer is known from the literature.[40] To distinguish the volume fraction determined using this method from the hard sphere volume fraction determined from small-angle scattering measurements, when used, it is referred to as ϕ_m.

Methods

Phase-analysis light scattering (PALS)

Electrophoretic mobilities were measured using a Malvern Zetasizer Nano Z or ZS with a universal dip cell electrode. The applied field strength used was either 1.0×10^4 V m^{-1} or 2.0×10^4 V m^{-1}, depending on the electrophoretic mobility of the sample being measured. The lowest field strength possible was used to avoid any effect of field dependent mobility.[27]

Six runs of at least 50 measurements were performed, and the average of these runs was used.

Small-angle neutron scattering (SANS)

Neutron scattering measurements were performed at the ISIS Pulsed Neutron Source. On Sans2d, a simultaneous Q-range of 0.003–0.43 Å^{-1} was achieved using an instrument set up with the source-sample and sample-detector distances of L_1=L_2=8 m and the 1 m^2 detector offset vertically 60 mm and sideways −290 mm.[41] The beam diameter was 8 mm. Raw scattering data sets were corrected for the detector efficiency, sample transmission and background scattering and converted to scattering cross-sections using the instrument-specific software, Mantid.[42] These data were placed on an absolute scale (cm^{-1}) using the scattering from a standard sample (a solid blend of hydrogenous and perdeuterated polystyrene).[43] Data have been fit to models as described in the text using the SasView small-angle scattering software package.[44]

Small-angle X-ray scattering (SAXS)

SAXS measurements were performed using the instrument I22 at Diamond Light Source. Samples were measured in 1 mm capillaries, and data were recorded on a PILATUS 2M detector. The sample-detector distance was 9.4 m, and two X-ray wavelengths were used (1.77 Å, 7 keV, Q = 0.001–0.11 Å^{-1} and 0.73 Å, 17 keV, Q = 0.003–0.27). Raw scattering data sets were radially integrated using YAX 2.0, a macro script for ImageJ.[45,46] Data have been fit to models as described in the text using the SasView small-angle scattering software package with data weighted by $|\sqrt{I(Q}|$.[44]

Results and Discussion

The effect that varying particle concentration, while maintaining a constant surfactant concentration, has on the charge of particles will be considered in several steps. Electrokinetic measurements will be discussed first to demonstrate how the electrophoretic mobility (μ) varies with the latex volume fraction (ϕ) for small ($<$ 100 nm diameter) latexes. Two possible origins for these differences will then be explored: surfactant partitioning or double layer overlap. Surfactant partitioning will be quantified using contrast-variation small-angle neutron scattering (CV-SANS) and small-angle X-ray scattering (SAXS), and double layer overlap will be quantified by modeling the electrokinetic data. By establishing the origin of the effect of varying the volume fraction on the electrophoretic mobility of small particles, it will be possible to consider these results in conjunction with electrokinetic measurements on larger particles to elucidate the effect that changing particle size has on the particle charge and ζ potential.

The electrophoretic mobility of a dispersion of small PMMA latexes was determined as a function of volume fraction ($4 \times 10^{-4} \lesssim \phi \lesssim 2 \times 10^{-1}$) at a constant surfactant concentration (100 mM AOT). The electrokinetic measurements were performed using PALS. This dispersions were chosen because the amount of scattered light from the small latexes enabled measurements to be performed up to high volume fractions and because, as can be seen in Figure 1, the magnitude of the electrophoretic mobility varies dramatically across the range of particle concentrations studied. The reduced mobility (μ/μ_0, where $\mu_0 = e/(6\pi\eta\lambda_B)$ and λ_B is the Bjerrum length, shown in Equation 1) is shown rather than the experimental mobility, to account for the viscosity of the AOT solution being greater than the pure solvent. The relative viscosities for the solutions (η_r) have been calculated using the Einstein relationship ($\eta_r = 1 + 2.5 \cdot \phi$),[47,48] which has been shown to be appropriate for AOT solutions in dodecane.[49]

For this system, the charge on the particles is indeed impacted by the addition of AOT surfactant. As as these latexes are charged by an external molecule, the decrease in mobility

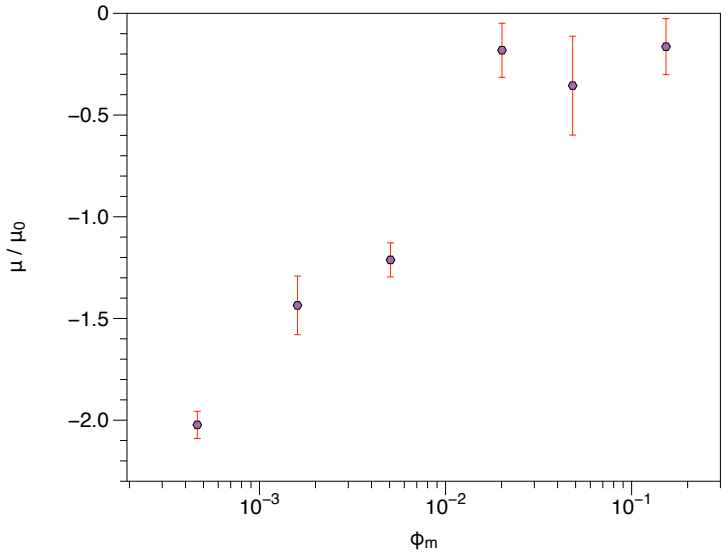


Figure 1: Reduced electrophoretic mobilities (μ/μ_0) of 76 nm PMMA latexes as a function of volume fraction (ϕ_m) at a constant AOT concentration of 100 mM. The magnitude of μ/μ_0 increases as the concentration of latexes decreases.

could be chemical or physical in origin. The possibility that this could arise from chemical interactions, namely the AOT reservoir being depleted by the large number of particles at large ϕ, will be explored first using small-angle scattering.

Surfactant interaction

As the particles are charged by interactions with an external species (AOT surfactant), the amount of surfactant incorporated into the particle will be an equilibrium. At fixed ϕ, the partitioning of AOT has recently been studied as a function of solution concentration.[10] The amount of surfactant absorption was found to vary as the solution concentration was changed, but the equilibrium constant of surfactant absorption was found to be constant.[10] In this study, the concentration of AOT is fixed while ϕ is varied. From previous studies in the literature, it is not possible to determine whether the amount of surfactant will be constant in each sample or not. This has been studied, using SANS and SAXS, for the small PMMA latexes used for the electrophoresis measurements in Figure 1. These latexes are used because they have previously been shown to be amenable to analysis by small-angle

scattering techniques.[10]

Dispersions without AOT

SAXS measurements were performed on the 76 nm latexes with no added surfactant and with 100 mM AOT added. As X-rays are sensitive to differences in electron density, the technique is sensitive only to the PMMA core of the latexes. (The PHSA stabilizer and AOT surfactant have essentially the same electron density as the dodecane solvent.) It is important to consider core-sensitive scattering as this enables a comparison of form factors ($P(Q)$) and structure factors ($S(Q)$) for latexes at different ϕ.

Figure 2 shows SAXS curves of 76 nm latexes at different volume fractions fit to a core-shell sphere form factor with a hard sphere factor.[50–53] The core radius (r_c) is allowed to vary, and the shell thickness (t_s) is fixed to 60 Å, the value used by Cebula *et al.*[50] The width of the distribution in the particle radii (σ_{Sch}) are accounted for using the Schulz distribution.[54] This model gives a very good fit to the data. (Best fit parameters are shown in the Supporting Information.) The form factor dimensions are constant for the three latexes ($r_c = 285$ Å and $\sigma_{Sch} = 0.10$). The fit volume fraction (ϕ_{fit}) for the most concentrated dispersion ($\phi_{\text{fit}} = 0.20$) is greater than calculated using the solid state densities ($\phi_m = 0.16$). While unexpected, this is perhaps not surprising. Determining the volume fraction of these latexes is known to be a challenging problem.[55] Volume fractions calculated using the solid state density assume that the latexes are a sphere with a fixed composite density, but in dispersions, the stabilizer chains will be highly solvated. This increases the apparent volume fraction (ϕ_{app}), which is the value that will be used for the remaining data presented. Using the dimensions from these SAXS measurements, it is possible to fix the dimensions used for fitting scattering curves when surfactant is added.

Before considering contrast-variation SANS (CV-SANS) measurements with added AOT-d_{34}, it is important to determine if there is any residual scattering in latex contrast-matched solvent. The scattering length density (SLD, ρ_{n}) of the latexes has been previously reported

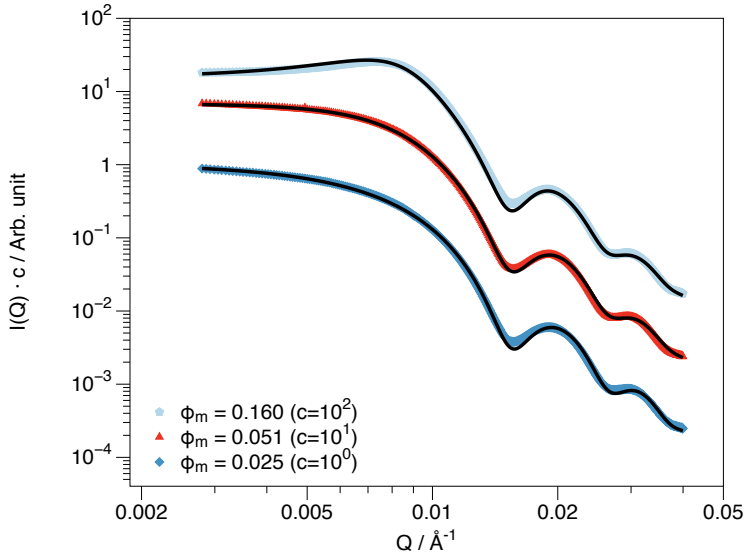


Figure 2: SAXS of 76 nm latexes in dodecane without AOT. The data are fit to a core-shell sphere form factor (with varying core radii and with a fixed 60 Å shell thickness) with a hard-sphere structure factor.[50–53] The data can be well fit using this model, demonstrating that these latexes interact essentially as hard spheres in the Q-range studied.

($\rho_n = 1.1 \times 10^{-6}$ Å^{-2}).[10,36] SANS has been measured for dispersions of 76 nm PMMA latexes in latex contrast-matched solvent (shown in Supporting Information). A non-negligible amount of scattering is observed, particularly for the most concentrated dispersion. This residual scattering, however, does not come from a mismatch between the solvent and the particle. The data can be very well fit assuming the scattering arises from the small amount of contrast between the PHSA stabilizer shells with the PMMA cores and the solvent.[36] The contribution of the PHSA polymer to SANS of these latexes was not considered in early studies on these latexes, due to limited Q-resolution and the latex-solvent contrasts arranged so that the PMMA core always dominted,[40,50] but recent SANS and spin-echo SANS studies show that the stabilizer polymer must be considered.[36,56] The SLD of the latexes (measured at a volume fraction of 0.02) corresponds to the SLD of the PMMA core, which dominates at low ϕ, but at high ϕ, the contribution from the shell needs to be considered as well.

Dispersions with AOT

Before interpreting SAXS and CV-SANS data of AOT-charged PMMA latexes, several points about the processing of the scattering curves need to be emphasized.

- As mentioned in the previous section, the PHSA polymer makes a small contribution to the total scattering curve, even in contrast-matched solvent. Using the properties of the dispersions measured while preparing them (exact volume fractions and solvent ρ_{n}), the residual scattering curves have been simulated and subtracted from the CV-SANS data (100 mM AOT-d_{34} with latexes in latex contrast-matched solvent).

- The 76 nm latexes are known to be charged by AOT (Figure 1), but a hard sphere structure factor is used to fit the data.[53] It is preferred over a charged sphere structure factor as it includes fewer parameters.[57,58] While more simplistic, due to the low ϵ_r of the solvent and consequently long Bjerrum length, charges interact over longer length scales than are probed in the Q-range accessed. The two structure factors result in fits of essentially the same quality. This can be seen in the inset of Figure 3a, which compares hard sphere and charged structure factors.

- The CV-SANS data is fit as a linear summation of two species: spherical AOT inverse micelles[59,60] and hard core-shell spheres.[50–52] This model does not account for the cross term that is observed in systems of binary spheres,[61,62] but it is preferred as a binary sphere model would neglect the contribution from the PHSA shell. This assumption does not significantly modify the scattering curves, however (shown in Supporting Information).

Having established the data processing method, the results from the scattering measurements can be considered. Figure 3 shows both SAXS data in unlabeled dodecane (Figure 3a) and CV-SANS in core contrast-matched dodecane (Figure 3b), and the best fit parameters to AOT-d_{34} absorbed in the latex core as determined from CV-SANS are shown in Table

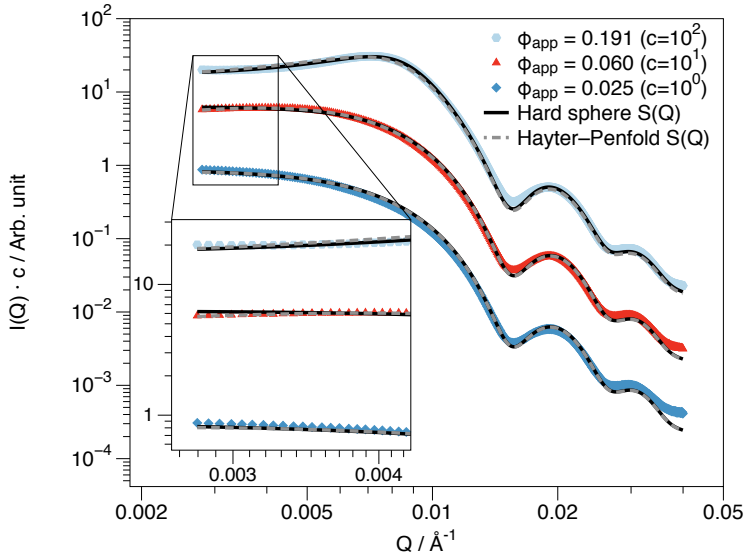
1. As the $S(Q)$ interactions arising from charged sphere interactions are shifted to lower-Q than can be detected using these configurations, only the microstructural detail that can be gleaned from the CV-SANS data will be discussed in detail.

Table 1: CV-SANS data fitting parameters for AOT-d_{34} and PMMA latexes.

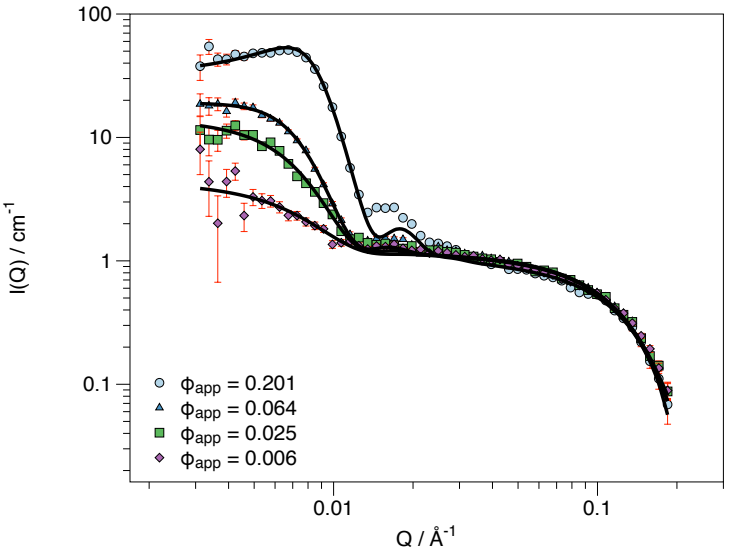
Volume fraction ϕ_{app}	r_c / Å	$\Delta\rho_{\text{n}}$ / (10^6 Å^{-2})
0.006	279	0.31
0.025	314	0.27
0.064	328	0.20
0.201	299	0.32

At high-Q, the scattering from AOT-d_{34} inverse micelles dominates, and the curves at different latex volume fractions overlap, as the same concentration of surfactant was added. At low-Q scattering from AOT-d_{34} absorbed in the PMMA latexes dominates. (The difference between *adsorption* and *absorption* of AOT surfactant has previously been discussed.[24]) The surfactant is considered to be homogeneously distributed throughout the latexes, a model that has recently been shown to describe this system well.[23,24] The size of the latex core is allowed to vary (see Table 1), as in a recent study on the distribution of double-chain and triple-chain charging agents, but this does not mean that the surfactant is located preferentially in any part of the latex. The data cannot be fit if the surfactant is *localized* in any region of the particle.[10] The intensity of the contribution from this component increases proportionally with the volume fraction of latexes. From a qualitative analysis of the data alone, it is not possible to tell whether this is due to a larger amount of surfactant being absorbed in the latexes or the same amount of surfactant being absorbed in a larger concentration of latexes. From the data fitting parameters shown in Table 1, it is clear that it is the latter case. The magnitude of $\Delta\rho_{\text{n}}$, which is indicative of the amount of surfactant that is absorbed, is essentially constant for the four volume fractions studied. This can be compared to the situation where ϕ is kept constant while the surfactant concentration is varied; $\Delta\rho_{\text{n}}$ decreases as the surfactant concentration is decreased.[10]

The amount of surfactant incorporated with the latexes, therefore, appears to be constant



(a) SAXS with AOT.



(b) CV-SANS with AOT.

Figure 3: Small-angle scattering, both SAXS (3a) and CV-SANS (3b), of dispersions of 76 nm PMMA latexes in solutions of 100 mM AOT (SAXS) or AOT-d_{34} (CV-SANS) as a function of volume fraction (ϕ_{app}). The SAXS measurements are sensitive to scattering from the PMMA core. Fits to the data show that the particles can be modeled successfully with a hard sphere $S(Q)$, although fits with a Hayter–Penfold $S(Q)$ for charged spheres are also shown. The CV-SANS measurements are performed in core contrast-matched dodecane and, thus, are sensitive only to the AOT-d_{34} surfactant. Fits to the data show that the scattering can be modeled well as a linear sum of constant concentration of inverse micelles (at high-Q) and surfactant absorbed in core-shell latexes (at low-Q).

as the volume fraction is varied. Higher concentrations of surfactant would have to be added to saturate the latexes, if it is even possible to reach this limit. A chemical origin for the mobility reduction, therefore, seems unlikely. The possibility that this could arise from physical interactions, namely the overlap of double layers at large number concentrations (n_i), will be explored next using electrokinetic modeling.

Electrokinetics

If the amount of AOT that is absorbed by the particles is volume fraction independent, then another explanation of the origin of the reduction in electrophoretic mobility must be sought. As was stated earlier, it is known in the literature that the electrophoretic mobility can decrease for otherwise identically charged particles as the dispersions are concentrated due to overlapping of the double layers.[31–35] The electrophoretic mobility has been calculated for each experimental ϕ with a varying ζ potential until the calculations best matched the entire set of data. As can be seen in Figure 4, using a constant, ϕ-independent ζ potential of -65 mV gives a very good match to the experimental data.

This provides an explanation for the reduction in electrophoretic mobility shown in Figure 1. There is sufficient surfactant to charge the particles, up to a volume fraction of $\sim 20\%$ at least. However, due to the overlap of the double layers, a consequence of having a large number concentration of particles filling this volume, the electrophoretic mobility is reduced and not constant. The ζ potential, however, is constant. This analysis shows that, for small particles at least, electrophoresis measurements over a range of volume fractions are required to determine the ζ potential. If any one of these samples were analyzed with an electrophoresis model that assumes infinite dilution, such as the Henry equation or the O'Brien and White method that are regularly used in studying charged colloids in nonpolar solvents,[63–65] the magnitude of the ζ potential would be underestimated. It is only when accounting for the volume fraction of the particles as well that the the correct ζ potential can be determined.

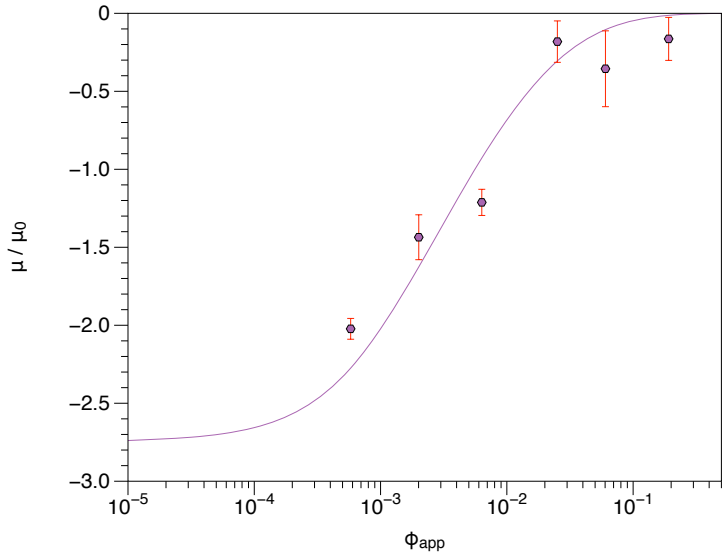


Figure 4: Reduced electrophoretic mobilities (μ/μ_0) of 76 nm latexes as a function of corrected volume fraction (ϕ_{app}). The data were previously shown in Figure 1. The values of μ/μ_0 were calculated assuming a constant ζ potential of -65 mV. This shows that the reduction of electrophoretic mobility at high volume fractions is due to the overlap of the double layers.

Extension to larger particles

The magnitude of the ζ potential for these 76 nm latexes is lower than has been found for AOT-charged PMMA latexes with a larger size, an observation that has been reported by a meta-analysis of the literature before.[26] Having performed these electrophoresis measurements at a wider range of volume fractions than previously reported in the literature, and consequently determining the ζ potential of the small particles with a larger amount of accuracy, it is worth considering if this can provide into insight into this observation. PALS measurements were performed on larger latexes as a function of volume fraction (shown in Supporting Information), although due to the greater amount of light scattered by these larger particles, it was only possible to perform measurements on dilute dispersions. At these volume fractions, the electrophoretic mobility is essentially concentration independent, perhaps with a slight decrease in magnitude for the most concentrated dispersions studied. The electrophoresis can be analyzed using the same model as used for the 76 nm latexes, and the volume fraction dependent electrophoretic mobility calculated assuming a constant ζ poten-

tial. As for the smaller latexes, the magnitude of the electrophoretic mobility decreases at higher volume fractions, although this is shifted to higher ϕ when the particles are larger. The magnitude of the ζ potential is also found to be greater (-95 mV for both). This agrees with an analysis of the literature,[26] although the difference in this study is lessened by accounting for the volume fraction.

These PMMA latexes have generally been considered to have a size-independent ζ potential, and a report in the literature studying a series of latexes using a single technique came to that conclusion.[8] These data suggest that this is not entirely the case but that very small latexes must be studied to see any difference. Large latexes do have a constant potential, but small latexes have a lower potential. What could the origin of this be?

There are models in the literature that report size dependent electrostatic properties for charged particles. Strubbe *et al.* found that surface potential and charge can depend on the size of the particle if the particles are charged by ionization equilibrium of surface sites and the number of surface sites decreases.[66] From the electrokinetic model used to analyze the electrophoresis of these latexes, the surface charge density can be determined as well as the ζ potential. The ζ potential is a volume fraction independent property, but the surface charge density decreases as ϕ increases. Therefore, the surface charge at a very low concentration ($\phi = 10^{-5}$) will be compared; at this concentration, the surface charge density has reached a asymptote. (The relation between surface charge density and volume fraction is shown in the Supporting Information.)

The ζ potential and the total surface charge Z are shown in Figure 5 as a function of size for the three latexes. As was discussed in the previous section, the ζ potential is lower for the smallest of the latexes, but it is the same for the larger latexes. The surface charge, however, is essentially a linear function of the radius. This is qualitatively the same as the observation of Strubbe *et al.*[66] For a near maximum number of surface sites, the charge is an approximately linear function of particle size, and the surface potential is constant for larger particles but decreases for the smallest particles. The similarity between the two studies

suggests that the charging of PMMA latexes by AOT surfactant in nonpolar solvents may be governed by the equilibrium of ionization at the surface. The surfactant may not entirely be located at the surface of the latexes. Our recent studies, along with this one, show that AOT surfactant appears to be absorbed in the core of the latexes.[10,23,24] However, it is the ionic groups at the surface that dictate the charge of the particle.

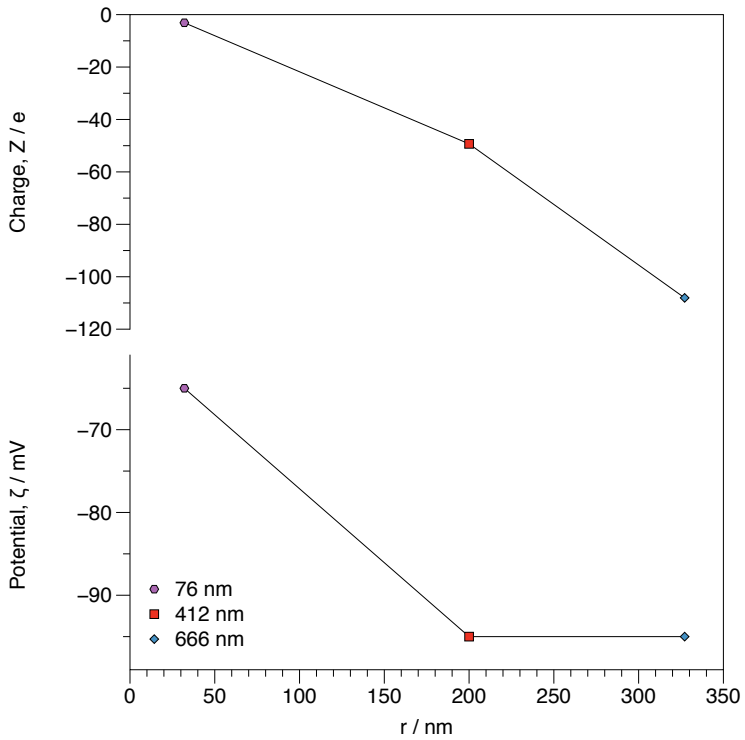


Figure 5: The surface charge Z and the ζ potential of PMMA latexes of different sizes (diameters given in the legend) at a constant AOT concentration of 100 mM. The charge is an approximately linear function of size, whereas the magnitude of the potential is greater for larger latexes than a small one.

Conclusions

The electrophoretic mobilities of dispersions of PMMA latexes charged by AOT surfactant have been studied as a function of particle volume fraction, a variable that has not been explored for this system before.[26] The mobility was found to decrease as the particle volume fraction was increased. Two possible origins for this were considered: the equilibrium

partitioning of surfactant between inverse micelles and PMMA latexes and the overlap of electrostatic double layers. Small-angle neutron scattering measurements showed that the amount of AOT-d_{34} absorbed into the latexes was independent of the volume fraction, and this was, therefore, not a viable explanation for the observation. In fact, the reduction in mobility is due to the overlap of the double layers, a consequence of the fact that small particles have a much greater number concentration than larger particles at the same volume fraction. This is the first study, as far as we are aware, to observe this for AOT-charged PMMA latexes. A reduction in the electrophoretic mobility for concentrated dispersions has been seen for ionic monomer charged latexes, caused by counterion condensation,[27] and for latexes charged by autoionized solvents, caused as in this study by double-layer overlap.[28]

This observation is significant for enabling accurate analysis of the electrophoresis of these types of particles. For small latexes, it is challenging to measure electrophoretic mobilities at dilute enough concentrations that the double layers do not interact. Performing measurements at a range of volume fractions and determining what ζ potential best matches the data, therefore, becomes a preferable way to characterize the electrokinetic data. From the data presented in this study, it appears that dispersions of the same latexes have a constant, volume fraction independent ζ potential. However, as has been proposed in a recent analysis of the literature on these PMMA latexes,[26] the potential does seem to vary as a function of particle size, whereas the surface charge is roughly linear. This correlates with theoretical analysis of the origin of the charging of particles being due to surface equilibria,[66] and this is an explanation that merits further study in the future.

The significance is not only relevant to studies of the fundamental electrokinetics of particles in nonpolar media. For particles used in applications, it is desirable to use concentrated dispersions to make efficient use of materials. Also, for application in electrophoretic displays,[3,67] for example, concentrated dispersions are desirable to maximize the amount of reflected light. However, concentrating the dispersions has a penalty, as the electrophoretic mobility of the particles is reduced, and particle motion is hindered. Therefore, for either

fundamental or applied studies of surfactant-charged particles in nonpolar solvents, the dependence of the particle charge on particle concentration must be appreciated to optimally use them.

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